

Rate constants for formation of NO in vibrational levels $v=2$ through 7 from the reaction $N(^4S) + O_2 \rightarrow NO^+ + O$

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Vibration-rotation spectra of the $4v = 2$ sequence of the nitric oxide formed by the chemiluminescent reaction $N(^4S) + O_2 \rightarrow NO(X^2II) + O$ have been obtained with a spectral resolution of 15 cm^{-1} . Emission bands due to N_2O were observed to occur in the same spectral region as the first overtone of NO. These were experimentally eliminated and the resulting NO spectra were used to derive rate constants for formation of NO in vibrational levels $v = 2$ through $v = 7$. In units of $10^{10} \text{ cm}^3/\text{sec}$, these room temperature rate constants are, respectively, 55 ± 14 , 57 ± 9 , 33 ± 3 , 24 ± 4 , 7 ± 2 , and 5 ± 2 . Of all the nitric oxide molecules formed in the reaction, only 18% are formed in levels $v \geq 2$. In terms of energy, of the 1.39 eV exothermicity of the reaction, about 10% goes into vibrational energy in levels $v \geq 2$.

I. INTRODUCTION

The reaction of ground state nitrogen atoms with oxygen molecules leading to formation of nitric oxide is of considerable interest in interpretation of auroral phenomena and more generally in determination of the degree of excitation of the product NO molecules. Infrared emission measurements are often useful in studying vibrationally excited products in chemiluminescent reactions. The technique was employed in this laboratory to study $N(^4S) + O_2 \rightarrow NO^+ + O$ (\dagger indicates vibrational excitation) under low spectral resolution.¹ In that experiment, it was shown that the reaction was chemiluminescent and from the envelope of the spectrally unresolved first overtone vibration-rotation bands of NO, some information regarding the excited state yield of the reaction was deduced. Subsequently, a photon efficiency figure for the reaction was reported.² In the analysis of the results of that investigation, the only loss mechanism for the NO molecules was assumed to be the very fast reaction $N + NO \rightarrow N_2 + O$. Estimates for the quenching rate of NO^+ by O_2 indicated this loss mechanism to be unimportant. It was also shown that in the pressure region employed, no redistribution among the vibrational levels occurred; whereas the NO rotational distribution quickly attained equilibrium with the gas mixture. The NO overtone band shapes could be described by independent vibrational and rotational temperature. Due to lack of resolution, unknown spectral features could not be distinguished and a molecular band at $\sim 2.25 \mu\text{m}$ could not be identified for the same reason. Since these early results, quenching of NO^+ by O_2 has been studied and measured by Murphy *et al.*, and is shown to be significant,³ Whitson *et al.*⁴ have also measured the quenching of NO^+ by O_2 and report rates for $v = 2$ through 7. In addition, they have reported an initial vibrational distribution for NO^+ from $N + O_2$ reaction using a slightly resolved experimental spectra of the NO overtone band.

More recently, the reaction of $N(^2D)$ with O_2 was studied by Kennealy *et al.*⁵ in a cold environment to suppress the $N(^4S) + O_2$ reaction whose rate constant exhibits a very large temperature dependence. Consequently, no information on the latter reaction was obtained, but values for the partial rate constants for the $N(^2D)$ reaction were reported.

To refine and augment the previous results obtained on $N + O_2$ reactions, the present interferometric study was undertaken to obtain resolved spectra of the NO first overtone, to identify the unknown molecular band referred to above, to ascertain that the NO emission bands were free from other molecular emissions, and finally to derive a set of detailed rate constants for formation of NO in level v , taking into account the quenching of vibrationally excited NO by O_2 .

Section II describes the experimental procedures and results. Section III is a discussion of these results and conclusions drawn from the experiment.

II. EXPERIMENTAL

A schematic of the experimental apparatus is shown in Fig. 1, which is essentially identical to that used in Ref. 1 with the exception that the circular variable filter was replaced by a Michelson interferometer-spectrometer for the purpose of obtaining the vibrational structure of the NO first overtone bands. Nitrogen atoms produced in the microwave cavity flow into the reaction vessel which is a 2 ft gold-coated integrating sphere with ports for pumping, gas admission, and pressure measurements. To increase the efficiency, the sphere was cleaned and freshly gold coated for this experiment. The nitrogen atom density as measured by the NO titration method was generally found to be approximately $7 \times 10^{13} \text{ cm}^{-3}$. Background molecular nitrogen pressure in the sphere was usually 250 mTorr. The oxygen pressure was varied over the range of 200 to 600 mTorr. Below this pressure, the signal to noise ratio was too low for meaningful measurements.

The interferometer was equipped with 1 in. optics and had a 1 cm maximum optical path difference as the continuously driven moveable mirror travelled between extreme positions. The central fringe was imaged by a $f/1.0$ silicon lens onto a $2 \times 2 \text{ mm}$ lead sulfide detector cooled to 193 K. The interferogram was digitized at successive intervals determined from the zero crossings of a 6328 Å He-Ne reference laser. Spectra were recovered by taking the Fourier transform of digitized interferograms. The instrument function was measured by observing the 4852.2 cm^{-1} helium line. Spectral re-

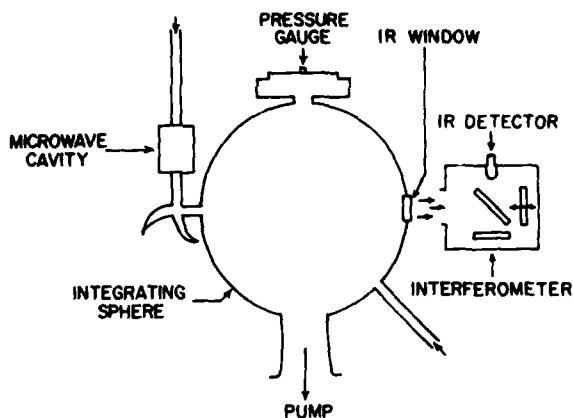


FIG. 1. Schematic diagram of the apparatus.

sponse was determined by calibration with a standard 1000 °C blackbody.

Several preliminary experimental runs to obtain resolved spectra of the first overtone of NO were made with the O_2 pressure fixed at 500 mTorr. A typical spectrum is shown in Fig. 2. Additional measurements over the oxygen pressure range of 200–600 mTorr produced spectra similar to the one shown. The appearance of the spectra in the 3100–3500 cm^{-1} region was persistently repeatable. Existence of these emission bands would indicate populating NO vibrational levels higher than allowed by 1.39 eV exothermicity of the reaction $N(^4S) + O_2 \rightarrow NO^+ + O$. Thus, the conclusion is that the bands in the 3100–3500 cm^{-1} region are due to species other than NO. This is supported by the observation of the band at 4450 cm^{-1} which is highly pronounced and is identified as the $00^02 - 00^00$ transition of the electronic ground state of N_2O . This is the band observed at 2.25 μm in the low resolution experiment.¹ The ν_3 mode of N_2O which occurs at 2225 cm^{-1} can also be discerned in Fig. 2 although the detector sensitivity in this region has fallen off considerably. The other two infrared fundamental modes at 1277 and 589 cm^{-1} (ν_1 and ν_2 , respectively) are entirely out of the spectral range of the detector. Nevertheless, other N_2O combination bands can overlap the NO first overtone range. In particular, bands at 3365 and 3481 cm^{-1} ,

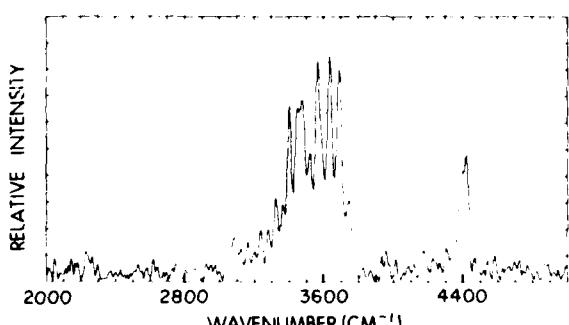


FIG. 2. Spectrum obtained at O_2 pressure of 500 mTorr. NO overtone spectral region is 3300 to 3800 cm^{-1} .

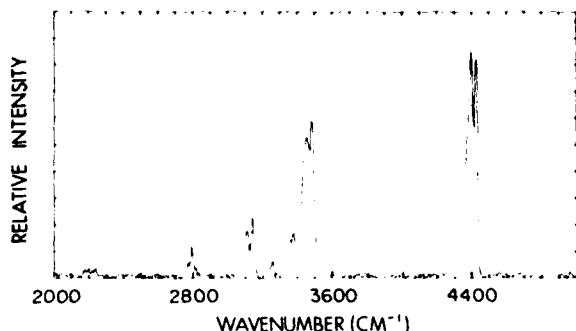


FIG. 3. N_2O spectrum obtained in vibrational exchange between pure N_2O and N_2^+ .

both being transitions to the (00^00) state of N_2O , would be expected to make radiative contributions and their existence is suggested in the spectrum shown in Fig. 2.

If N_2O is either formed chemically or exists in the chamber as trace impurity, the existence of copious amounts of vibrationally excited nitrogen (N_2^+) in the reaction cell suggests a possible source for the N_2O vibrational energy since N_2O undergoes rapid vibrational exchange with N_2^+ as shown in other investigations.^{6,7}

Figure 3 shows an N_2O infrared spectrum obtained in vibrational exchange with N_2^+ . The spectrum was obtained by adding ≈ 2 mTorr of N_2O to discharged nitrogen. All the spectral features are attributable to N_2O . Comparison of Fig. 2 and 3 provides strong evidence that vibrational exchange between N_2^+ and N_2O also occurs in the $N(^4S) + O_2 \rightarrow NO + O$ experiment of Fig. 2.

The bands at 2225 and 4445 cm^{-1} , which were referred to above, are the ν_3 and $2\nu_3$ modes of N_2O , respectively. The former is in close energy resonance ($\Delta E = 107 \text{ cm}^{-1}$) with N_2 ($r=1$) and the latter ($\Delta E = 210 \text{ cm}^{-1}$) is attributed to either direct exchange with N_2 ($r=2$) or further exchange between N_2O (00^01) and N_2 ($r=1$) resulting in N_2O (00^02). Tentative identification of some of the other observed bands include the combination bands ($\nu_1 + \nu_3$) at 3480 cm^{-1} and $(2\nu_2 + \nu_3)$ at 3365 cm^{-1} . The two bands at about 3260 and 3150 cm^{-1} could be $2(\nu_3 - \nu_2)$ and $(2\nu_3 - \nu_1)$, respectively, and the band at 2800 cm^{-1} is $(\nu_2 + \nu_3)$.

Precautions were taken to assure that none of the gas supplies contained N_2O . Trapping at 77 K of the high purity research grade gases over prolonged periods produced no reduction in N_2O emissions. Spectra of discharged nitrogen were also obtained and no N_2O bands were observed, indicating it was not present or formed in the discharge flow system. All evidence points to chemical formation of N_2O when O_2 and active nitrogen are mixed.

Since vibrationally excited nitrogen (N_2^+) is the source of N_2O vibrational energy, quenching of the N_2^+ indeed eliminated all N_2O signals. This quenching was accomplished by insertion of sufficient amounts of Pyrex wool in the discharge prior to gas flow entrance into the reaction cell. This procedure is known to quench the vibrationally excited N_2 with some reduction of N density.⁸

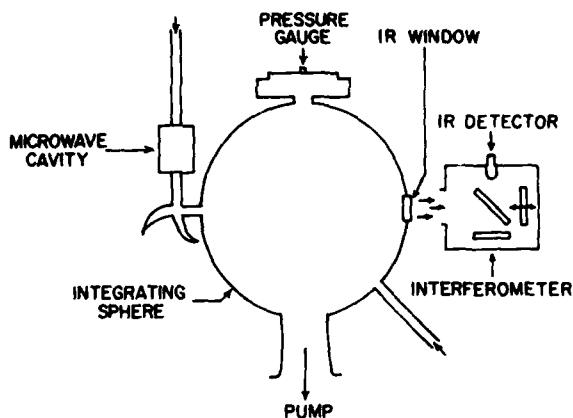
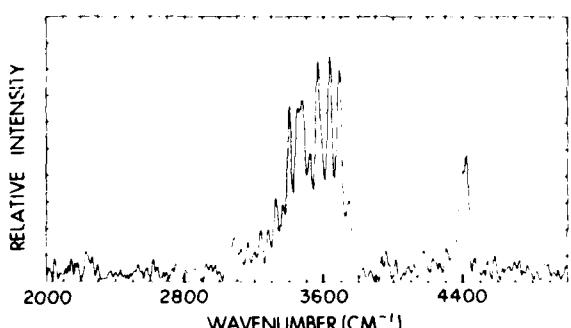
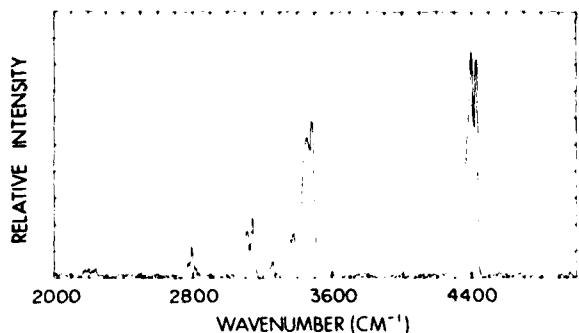


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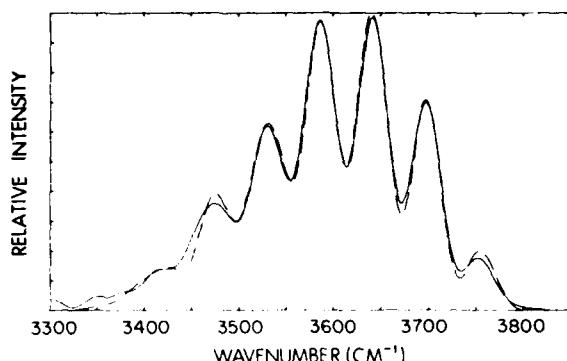


FIG. 4. NO first overtone spectrum obtained at O_2 pressure of 500 mTorr. The dashed curve is calculated for best fit to the experimental result (solid curve).

Figure 4 shows the overtone band of NO obtained after elimination of N_2O emission bands in the manner just described. Although only the limited spectral range of NO overtone is shown in this figure, the N_2O bands outside this spectral range were also absent. The spectrum which is corrected for the spectral response of the optical system is a sample of results obtained over the O_2 pressure range of 200 to 600 mTorr and forms the basis of the analysis of results in the next section.

N_2O emission occurring in the overtone region of NO was undetectable in the low resolution experiment due to the smoothing effect of the scanning function of the circular variable filter employed in the experiment.¹ As a result, the value of NO overtone photons per O_2 molecules reported to be 1.5×10^{-6} in Ref. 1 has to be corrected for contribution due to N_2O emission. The method used was to obtain the spectra with and without Pyrex wool in the discharge side of the reaction cell. Comparison of the two areas under the two spectra then furnished the relative magnitude of the N_2O and NO emissions. We found that nearly 1/3 of the signal observed was due to N_2O . This ratio was nearly the same over the O_2 pressure range used. Thus, the rate of photon production per O_2 molecule is revised down to 10^{-6} from its reported value.¹ This quantity will be used in the next section to derive NO(v) number densities.

An estimate of the density for N_2O can also be obtained from the relative magnitude of the 4450 cm^{-1} band of N_2O in Figs. 2 and 3. This indicated a density of $5 \times 10^9\text{ cm}^{-3}$ for N_2O at an O_2 pressure of 500 mTorr. This is only meant as an estimate since the finite pressure of oxygen molecules at the experimental conditions under which Fig. 2 was obtained may modify the nitrogen vibrational distribution. A possible mechanism for N_2O formation will be considered later in this paper. The fact that no N_2O emission was seen after elimination of N_2^{\ddagger} from the discharge indicates that the vibrationally excited N_2 from $N + NO - N_2^{\ddagger} + O$ is not produced at sufficient quantities to contaminate the NO spectra.

III. RESULTS AND DISCUSSION

To obtain the observed distribution from the experimental spectra (solid curve in Fig. 4) the procedure

was to simulate the NO observed spectrum, in a manner similar to the method used by Kennealy *et al.*⁵ At each O_2 pressure, the observed spectrum was simulated through a computer program that involved calculation of line positions and intensities for each vibration-rotation band from $v = 2$ through $v = 7$, and convolution of each band with the experimentally determined scanning function of the interferometer. The relative intensities of the NO vibration-rotation bands were fit to give the best match to the observed spectrum by multiple linear regression analysis. This simulated spectrum is shown as the dashed curve in Fig. 4 and is the calculated spectrum for the observed one shown in that figure.

The total photon emission rate of 10^6 per s per O_2 molecule¹ and a set of Einstein transition probabilities calculated by Billingsley⁶ were used to convert the relative observed distribution into NO number densities. The results for the entire set of experimental spectra are shown in Table I. Extensive calculation of the error in these number densities has shown that the experimental error of 30% in photon measurements is the dominant factor and is propagated through to the number densities in Table I.

The reaction $N(^4S) + O_2 \rightarrow NO(v) + O$, based upon exothermicity arguments, can only populate up to and including level $v = 6$ of the product NO. Formation of NO in the $v = 7$ level is due to available kinetic energy in the relative energy distribution of the reactants beyond the activation energy. Our calculations show that this energy is sufficient to make the $v = 7$ level accessible to the product NO molecule.

Derivation of the partial rate constants from densities shown in Table I is made complicated by the fact that the nitrogen atom density in the sphere does not remain constant and varies over the residence time in the sphere of 0.5 s. Consequently, NO densities vary as functions of time. Thus, the observed densities in Table I are values time averaged over the residence time in the reaction cell and further analysis of the results requires knowledge of this variation for each level v . To do this, the important reactions influencing NO density have to be determined.

Kinetic mechanisms of importance in this experiment are

TABLE I. Observed NO densities^a for $v = 2$ through 7.

O_2 pressure (mTorr)	NO(v)					
	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$	$v = 7$
200 ^b	1.15	1.03	0.65	0.40	0.12	0.05
250 ^b	1.30	1.10	0.75	0.39	0.18	0.05
300 ^b	1.68	1.64	0.92	0.52	0.15	0.07
400 ^b	2.34	2.05	1.08	0.63	0.22	0.09
440 ^b	2.82	2.51	1.25	0.68	0.19	0.09
510 ^b	3.27	2.85	1.48	0.76	0.25	0.11
600 ^c	3.16	2.84	1.73	0.97	0.27	0.10

^aDensities in powers of 10^9 molecules cm^{-3} .

^bDensities are averages of two runs.

^cDensities are averages of five runs.

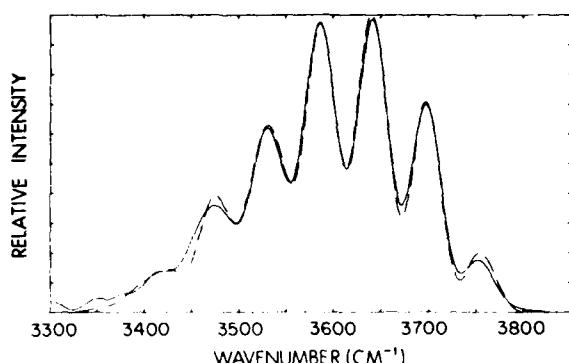


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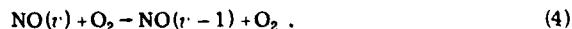


followed by the fast reaction



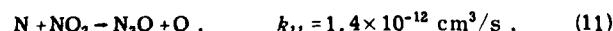
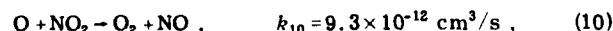
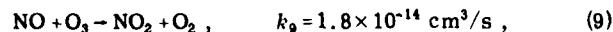
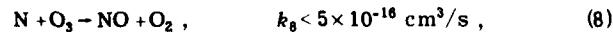
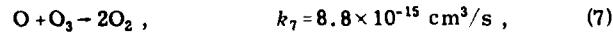
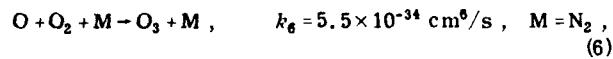
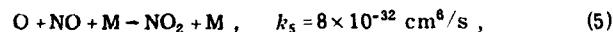
The rate constant for Reaction (1) is dependent upon the vibrational level of the product NO molecule and is denoted by $k_1(r)$, the detailed rate constant. The total rate $\sum k_1(r)$ is k_1 , which has a room temperature rate of 10^{-16} cm³/s.¹⁰

Reaction (2), which had an accepted rate constant of 2.2×10^{-11} cm³/s,¹¹ has been studied recently by Lee *et al.*,¹² who report a value of 3.4×10^{-11} cm³/s. Since no concrete information concerning the dependence of k_2 on vibrational level r of the NO molecule is presently available, in the present analysis it is assumed to be independent of r . In view of the large exothermicity of Reaction (2) this assumption is probably not drastic. NO density of level r is also dependent upon quenching by O₂:



Reaction (3) is a production mechanism for NO(r) and Reaction (4) is a loss mechanism with quenching rates denoted by $k_q(r+1)$ and $k_q(r)$, respectively. Values for these were taken from Refs. 3 and 4, and range from 2.4×10^{-14} cm³/s for $r=2$ to 8.6×10^{-14} cm³/s for $r=3$. Quenching of NO(r) by N₂ can be neglected since its rate constant is reported to be two orders of magnitude smaller than that of O₂.³

Other reactions occurring among various atoms and molecules that could affect the NO density measurements are listed below along with their room temperature rate constants:



The listed rates for Reactions (5), (6), and (7) are taken from Refs. 13, 14, and 15, respectively. The quoted value of the rate for Reaction (8) is an upper limit placed upon the rate in the recent experiment by Stief *et al.*¹⁶ The rates of Reaction (9) is one recommended in Ref. 17. Rates for Reactions (10) and (11) are taken from Refs. 18 and 19, respectively. One point that must be emphasized in regards to Reaction (11) is that the listed path going to products N₂O and O is the only channel detected by Clyne and McDermid,¹⁹ and is also the only reaction in this kinetic scheme that leads to formation of N₂O.

In order to assess the relative importance of Reactions (5) through (11) and their contributions to NO densities through Reactions (8) and (10), some estimate

of the densities of (N), (O), (NO), etc. is needed. The initial maximum number density of N atoms is $7 \times 10^{13}/\text{cm}^3$ and decreases with time at each oxygen pressure due to chemical reaction. Reactions (1) and (2) are dominant loss mechanisms for nitrogen atoms and the lifetimes of NO molecules against destruction by N atoms, given by $(k_2 N)^{-1}$, is less than 10^{-3} s and thus NO will be in quasi-steady state over the residence time of 0.5 s with its concentration given by $NO = (k_1/k_2) O_2$. Accordingly, at the highest oxygen density of about $2 \times 10^{16}/\text{cm}^3$ the NO density in the reaction cell will be less than $10^{11}/\text{cm}^3$. This is a maximum value for total NO density. Behavior of oxygen atoms is governed by Reactions (1), (2), (5)-(7), and (10) and with maximum NO concentrations given above it can be seen that the dominant loss mechanism for O atoms is Reaction (6) with a time constant of $(k_6 O_2 M)^{-1}$ which at O₂ pressures used is several seconds. Thus, O-atom concentration will not be in steady state and for times on the order of the residence time will be approximately given by $2k_1(N)(O_2)/t$, varying linearly with time. For residence time of 0.5 s, this yields a value of $1.4 \times 10^{14}/\text{cm}^3$ for O-atom concentration. Based upon these values of N, O, and NO concentration, it can easily be shown that both Reactions (8) and (9) can be neglected relative to Reaction (7), i.e., ozone formed in Reaction (6) reverts back to O₂ in recombination with oxygen atoms.

Maximum O₃ concentration itself can be gotten from Reactions (6) and (7) and using maximum O concentration obtained above. This yields a value of $(O_3)_{max} \approx 10^{13}/\text{cm}^3$. It is now obvious that $N + O_3 \rightarrow NO + O_2$ [i.e., Reaction (8)] as a source of NO is totally negligible compared to Reaction (1). Experimental evidence in the present experiment supporting this conclusion is the fact that levels higher than $r=7$ were absent in the NO spectra, whereas Reaction (8) with exothermicity of ≈ 4 eV can populate NO to levels approaching $r=20$. Of the two production mechanisms for NO₂, it can be easily seen that Reaction (5) dominates Reactions (9) and (10) as a destruction mechanism for NO₂ dominates Reaction (11). Calculations show that NO₂ densities are on the order of $(0.7-1) \times 10^7/\text{cm}^3$ and thus Reaction (10) as a potential source of NO is completely negligible relative to Reaction (1). Three body recombinations such as $N + O + M \rightarrow NO + M$ and nitrogen atom recombination on the wall can also be neglected on the time scales of interest. As regards diffusion effects on the results, calculations using the available diffusion coefficient for N in N₂^{20,21} show that the diffusion depth at pressures used in the experiment is much longer than the dimensions of the chamber such that complete homogeneous mixing has occurred. The effect of the walls on the vibrationally excited NO is difficult to assess but it can perhaps be estimated as follows: The lifetime of an NO molecule against destruction by nitrogen atoms is less than 1 ms (see above). For this time the diffusion distance at the pressures used is on the order of 1 cm. Assuming that one half of the vibrationally excited NO molecules within this distance to the walls are deactivated there, the loss would amount to less than 5% and will be less if the wall is not as efficient in deactivation as assumed.

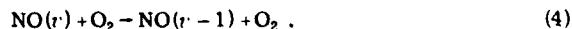


followed by the fast reaction



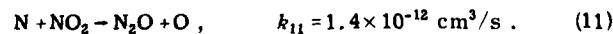
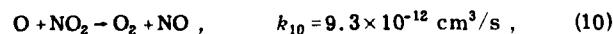
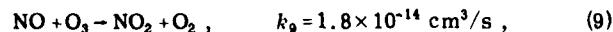
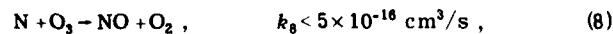
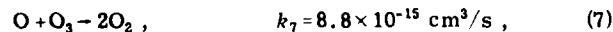
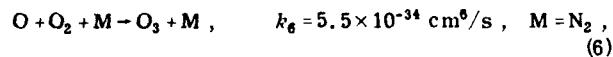
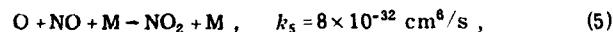
The rate constant for Reaction (1) is dependent upon the vibrational level of the product NO molecule and is denoted by $k_1(r)$, the detailed rate constant. The total rate $\sum k_1(r)$ is k_1 , which has a room temperature rate of 10^{-16} cm³/s.¹⁰

Reaction (2), which had an accepted rate constant of 2.2×10^{-11} cm³/s,¹¹ has been studied recently by Lee *et al.*,¹² who report a value of 3.4×10^{-11} cm³/s. Since no concrete information concerning the dependence of k_2 on vibrational level r of the NO molecule is presently available, in the present analysis it is assumed to be independent of r . In view of the large exothermicity of Reaction (2) this assumption is probably not drastic. NO density of level r is also dependent upon quenching by O₂:



Reaction (3) is a production mechanism for NO(r) and Reaction (4) is a loss mechanism with quenching rates denoted by $k_q(r+1)$ and $k_q(r)$, respectively. Values for these were taken from Refs. 3 and 4, and range from 2.4×10^{-14} cm³/s for $r=2$ to 8.6×10^{-14} cm³/s for $r=3$. Quenching of NO(r) by N₂ can be neglected since its rate constant is reported to be two orders of magnitude smaller than that of O₂.³

Other reactions occurring among various atoms and molecules that could affect the NO density measurements are listed below along with their room temperature rate constants:



The listed rates for Reactions (5), (6), and (7) are taken from Refs. 13, 14, and 15, respectively. The quoted value of the rate for Reaction (8) is an upper limit placed upon the rate in the recent experiment by Stief *et al.*¹⁶ The rates of Reaction (9) is one recommended in Ref. 17. Rates for Reactions (10) and (11) are taken from Refs. 18 and 19, respectively. One point that must be emphasized in regards to Reaction (11) is that the listed path going to products N₂O and O is the only channel detected by Clyne and McDermid,¹⁹ and is also the only reaction in this kinetic scheme that leads to formation of N₂O.

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of the densities of (N), (O), (NO), etc. is needed. The initial maximum number density of N atoms is $7 \times 10^{13}/\text{cm}^3$ and decreases with time at each oxygen pressure due to chemical reaction. Reactions (1) and (2) are dominant loss mechanisms for nitrogen atoms and the lifetimes of NO molecules against destruction by N atoms, given by $(k_2 N)^{-1}$, is less than 10^{-3} s and thus NO will be in quasi-steady state over the residence time of 0.5 s with its concentration given by $NO = (k_1/k_2) O_2$. Accordingly, at the highest oxygen density of about $2 \times 10^{16}/\text{cm}^3$ the NO density in the reaction cell will be less than $10^{11}/\text{cm}^3$. This is a maximum value for total NO density. Behavior of oxygen atoms is governed by Reactions (1), (2), (5)-(7), and (10) and with maximum NO concentrations given above it can be seen that the dominant loss mechanism for O atoms is Reaction (6) with a time constant of $(k_6 O_2 M)^{-1}$ which at O₂ pressures used is several seconds. Thus, O-atom concentration will not be in steady state and for times on the order of the residence time will be approximately given by $2k_1(N)(O_2)/t$, varying linearly with time. For residence time of 0.5 s, this yields a value of $1.4 \times 10^{14}/\text{cm}^3$ for O-atom concentration. Based upon these values of N, O, and NO concentration, it can easily be shown that both Reactions (8) and (9) can be neglected relative to Reaction (7), i.e., ozone formed in Reaction (6) reverts back to O₂ in recombination with oxygen atoms.

Maximum O₃ concentration itself can be gotten from Reactions (6) and (7) and using maximum O concentration obtained above. This yields a value of $(O_3)_{max} \approx 10^{13}/\text{cm}^3$. It is now obvious that $N + O_3 \rightarrow NO + O_2$ [i.e., Reaction (8)] as a source of NO is totally negligible compared to Reaction (1). Experimental evidence in the present experiment supporting this conclusion is the fact that levels higher than $r=7$ were absent in the NO spectra, whereas Reaction (8) with exothermicity of ≈ 4 eV can populate NO to levels approaching $r=20$. Of the two production mechanisms for NO₂, it can be easily seen that Reaction (5) dominates Reactions (9) and (10) as a destruction mechanism for NO₂ dominates Reaction (11). Calculations show that NO₂ densities are on the order of $(0.7-1) \times 10^7/\text{cm}^3$ and thus Reaction (10) as a potential source of NO is completely negligible relative to Reaction (1). Three body recombinations such as $N + O + M \rightarrow NO + M$ and nitrogen atom recombination on the wall can also be neglected on the time scales of interest. As regards diffusion effects on the results, calculations using the available diffusion coefficient for N in N₂^{20,21} show that the diffusion depth at pressures used in the experiment is much longer than the dimensions of the chamber such that complete homogeneous mixing has occurred. The effect of the walls on the vibrationally excited NO is difficult to assess but it can perhaps be estimated as follows: The lifetime of an NO molecule against destruction by nitrogen atoms is less than 1 ms (see above). For this time the diffusion distance at the pressures used is on the order of 1 cm. Assuming that one half of the vibrationally excited NO molecules within this distance to the walls are deactivated there, the loss would amount to less than 5% and will be less if the wall is not as efficient in deactivation as assumed.

The major conclusion of the above arguments is that the only reactions that have to be taken into consideration in the analysis of the data of Table I are Reactions (1) through (4). The effect of not taking into account the quenching Reactions (3) and (4) will be discussed below. The rate of change of NO density in vibrational level v is thus given by

$$\frac{d(NO)_v}{dt} = k_1^v(N)(O_2) - k_2(N)(NO)_v + k_q^{v+1}(O_2)(NO)_{v+1} - k_q^v(O_2)(NO)_v. \quad (12)$$

There are six such rate equations, one governing the density in each level v . Nitrogen atom density (N) itself is time dependent as mentioned above. The rate equation governing (N) can be evaluated from Reactions (1) and (2). The computer program developed for solution of Eq. (12) first solves for this time dependence of N density and then utilizes the Runge-Kutta method of order 4 for solving simultaneous differential equations.²² This method, which is essentially an iterative technique, requires (a) a starting set of values for k_1^v 's, and (b) initial values for NO concentrations. For the starting values of the rate constants we chose the solutions of Eq. (12) assuming steady state and neglecting the O_2 quenching terms. The initial $(NO)_v$ concentrations are, of course, all equal to zero. The computer program then using these values calculates the time history of NO for each level v and each oxygen pressure employed. It then calculates the time average for each $(NO)_v$ over residence time of 0.5 s for comparison with the experimentally obtained values listed in Table I.

Several other quantities in Eq. (12), such as $[d(NO)_v/dt]$, N , and $(N)(NO)_v$, are also calculated, time averaged, and tabulated. If the calculated time average of each $(NO)_v$ did not agree with experimental values, the procedure was repeated with a new set of k_1^v obtained from Eq. (12) by insertion of the time averaged quantities $(d/dt)(NO)_v$, (N) , and $(N)(NO)_v$ and experimental values of Table I into Eq. (12). With this new set of k_1^v the procedure was iterated and it generally took 20 to 25 iterations before convergence was obtained, and final rates arrived at. These final values for vibrational rate constants are shown in Table II and Fig. 5 shows the time variation of NO vibrational densities at O_2 pressure of 500 mTorr using rates shown in Table

TABLE II. Partial rate constants for formation of vibrationally excited NO in the $N(^4S) + O_2 \rightarrow NO^+ + O$ reaction.

v	k_1^v (cm ³ /s)
2	55 ± 14 (- 19)
3	57 ± 9
4	33 ± 3
5	24 ± 4
6	7 ± 2
7	5 ± 2

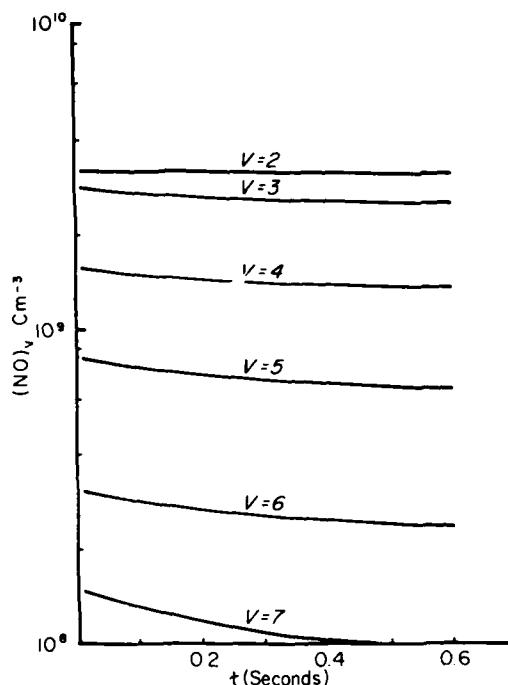


FIG. 5. Time variation of NO concentrations for the observed levels $v = 2$ through 7 and using the measured values of k_1^v shown in Table II.

II. The initial rise of this curve from zero, which is primarily determined by the time constant $(k_2 N)^{-1}$ ($\approx 10^{-3}$ s), is not shown in Fig. 5 for clarity. The uncertainties in the rate constants shown in Table II are the results of propagation of error calculations and include uncertainties in band intensity determination and photon emission rates. The large errors in the rate for levels 2 and 3 are probably due to absorption by water vapor in the optical path of the interferometer. Levels 6 and 7 often had poor S/N ratios especially at low O_2 pressure and consequently show large uncertainties in their rates. The sum of the rates in Table II is 0.18×10^{-16} cm³/s, which compared to the total rate of formation of NO of 10^{-16} cm³/s shows that only 18% of all NO product molecules are initially formed in levels $v > 2$ while the remainder of the 82% is shared in levels $v = 0$ and 1. The sum of the rates for these two levels is 0.82×10^{-16} cm³/s and at the present time there is nothing in the experiment to point to individual rates for levels $v = 0$ and 1. Considering the observed levels $v = 2$ to 7, from the point of view of energy, of the 1.39 eV exothermicity of the $N + O_2 \rightarrow NO + O$ reaction, only about 0.14 eV or 10% shows up in vibrational energy levels $v > 2$. The overall result then is that the reaction does not populate the higher vibrational levels of the product NO molecule effectively.

This general result has been independently confirmed by Whitson *et al.*⁴ in their experiment which measured only relative values for initial vibrational distribution. Their results basically exhibit the same value for the first four observed levels whereas the present results, except for $v = 2$, monotonically decrease as a function

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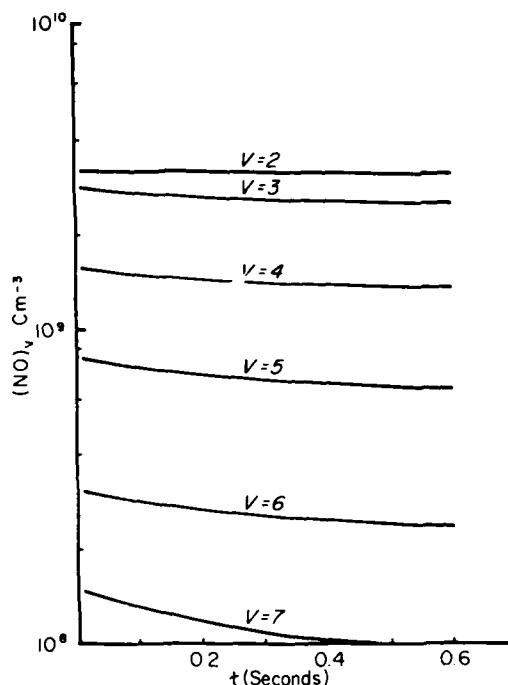


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of vibrational level v . The derived values of the vibrational rate constants remain the same to within a few percent when the initial number density of nitrogen atoms N_0 is allowed to vary in the computational program by as much as $\pm 50\%$. This is gratifying and shows that errors in determining N_0 by titration have no effects on the final results. We have also shown that neglecting the experimental values of the NO concentrations at higher pressures (500 mTorr and up) from the calculations had negligible effect on k_1^v for all levels and, of course, this would tend to confirm our conclusion above regarding diffusion. If the quenching terms in Eq. (12) are dropped from the calculation, the resulting values of k_1^v vary by as much as 20% for most levels and thus, in experiments involving the reaction of $N(^4S)$ with O_2 , the quenching of the product NO by O_2 cannot be neglected. The quenching of $NO(v)$ by oxygen atoms can have similar effect on the results. Since this quenching rate is not available for all vibrational levels, the effect can be estimated by assuming the rate to be invariant with v and equal to that of $NO(v=1) + O \rightarrow NO(v=0) + O$, which has recently been measured to be $6.5 \times 10^{-11} \text{ cm}^3/\text{s}$.²³ Assuming single quantum transitions, calculation yielded the following values (in $10^{-19} \text{ cm}^3/\text{s}$) for k_1^v : 61, 80, 47, 38, 10, and 8 for $v=2$ through $v=7$, respectively. Comparison with values in Table II shows that with oxygen atom quenching included, NO formation rate constants are increased and increases are slightly larger for higher vibrational levels.

Regarding the mechanism responsible for formation of N_2O , this molecule can possibly be formed in the standard kinetic mechanism of Reaction (5) forming NO_2 which in turn reacts with N to form N_2O via Reaction (11). The resulting concentrations of N_2O calculated based upon this mechanism appear to be a factor of 5 lower than the observed concentration quoted above which may be in error anyway (see above).

Finally, to summarize, we have measured the vibrational rate constants for formation of NO in levels $v=2$ through $v=7$ in $N(^4S) + O \rightarrow NO + O$ reaction. Unfortunately, there are no other absolute measurements of these rates for comparison with our results. We have made reasonably sure that our observations indeed measured emission from NO formed in this reaction and that spectral contamination was eliminated. Nevertheless, further research is needed. It appears that measurement of these rates through observation of the NO fundamental at $5.4 \mu\text{m}$ would be very illuminating in addition to providing rate constants for ground and first vibrational levels.

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